

INNOVATIVE SELF HEALING SEALS FOR SOLID OXIDE FUEL CELLS (SOFC)

Prof. Raj N. Singh

**Energy and Materials Engineering
University of Cincinnati, Cincinnati
OH 45221-0012**

**Supported by DOE-SECA Program and University of Cincinnati
(Dr. Joseph Stoffa, Project Manager)**

12th Annual SECA Workshop, Pittsburgh, July 28, 2011



Raj Singh-2011



ACKNOWLEDGMENTS

- **SECA Core Technology for Program Support**
Joe Stoffa, and Travis Shultz for Program Management and Guidance on the Project
Shailesh Vora for Discussions on Seals
Chris Johnson of NETL for help with in situ x-ray diffraction at high temperature.
- **S. Singh and N. Govindaraju at UC for help with experiments**
- **PNNL, Ceramatec , and University of Utah for Samples**
Matt Chou, Jeff Stevenson, P. Singh, S. Elangovan and Anil Virkar
- **FuelCell Energy, Delphi and GE Power Systems for Guidance and Industry Perspective**
N. Minh, Pinakin Patel, and Diane England



INTRODUCTION

- **Requirements of Seals for SOFC**

- ◆ Electrochemical-insulating to avoid shorting
- ◆ Lowest possible thermomechanical stresses upon processing, during heat up, cool down, and in steady state/transient operations
- ◆ Long life (40,000h) under electrochemical and oxidizing/reducing environments at high temperatures $\sim 600-850^{\circ}\text{C}$
- ◆ Low cost

- **Type of Seals**

- ◆ Ceramic-Ceramic (Electrolyte-Ceramic Insulator)
- ◆ Ceramic-Metal (YSZ-Ferritic Steel)
- ◆ Metal-Metal
- ◆ Rigid and/or Compliant
- ◆ Chemical/Mechanical/Liquid



A SELF-HEALING/REPAIRABLE SEALING CONCEPT FOR SOFC

- **Rationale:** A glass of appropriate characteristics can self-heal the cracks created upon thermal cycling and/or stresses created during SOFC operation. In addition, thermomechanical incompatibilities between ceramic and metallic materials requiring seals/joining can be alleviated using a self-healing glass seal.
- **Advantages:** The leaks developed upon SOFC operation and thermal cycling can be repaired in situ by the self-healing concept.
- **Challenges:** Develop appropriate glasses which satisfy thermomechanical and thermochemical compatibilities, remain stable for long-time against crystallization, and maintain self-healing/repairability capability.
- **Approach:** Thermophysical and thermochemical property measurements and glass optimization, self-healing ability, and leak testing to demonstrate self-healing/repairable seals.



CURRENT PROGRAM OBJECTIVES AND ACCOMPLISHMENTS

● **Phase-I: Objectives** (October 2009-March 2011)

- ◆ Demonstrate control of self-healing glass flow via addition of fillers for use as seals for SOFCs
- ◆ Develop self-healing glass-composites containing fillers for functionality as seals for SOFCs
- ◆ Select appropriate filler materials suitable for making glass-composites
- ◆ Characterize thermomechanical properties of glass-composites
- ◆ Measure stability of the self-healing glass-composites in SOFC environments
- ◆ Assess stability of the glass-composites in contact with YSZ

● **Accomplishments**

- ◆ Selected Alumina, Magnesia, and YSZ as fillers for making glass-composites
- ◆ Measured thermomechanical properties of glass-composites
- ◆ Demonstrated response of self-healing glass-composites over a range of temperatures between 25-800°C and identified promising filler materials
- ◆ Down-selected YSZ filler for making promising glass-composites and assessed stability of glass-YSZ composites in SOFC environments for 1000h
- ◆ These results provide great promise towards meeting SECA goals of seals for SOFC.



EXPERIMENTAL

- **Materials**

- ◆ Fillers Selected Alumina, Magnesia, and YSZ
- ◆ Self-Healing Silicate Glass

- **Fabricate Glass-Composites Displaying Self-Healing Behavior**

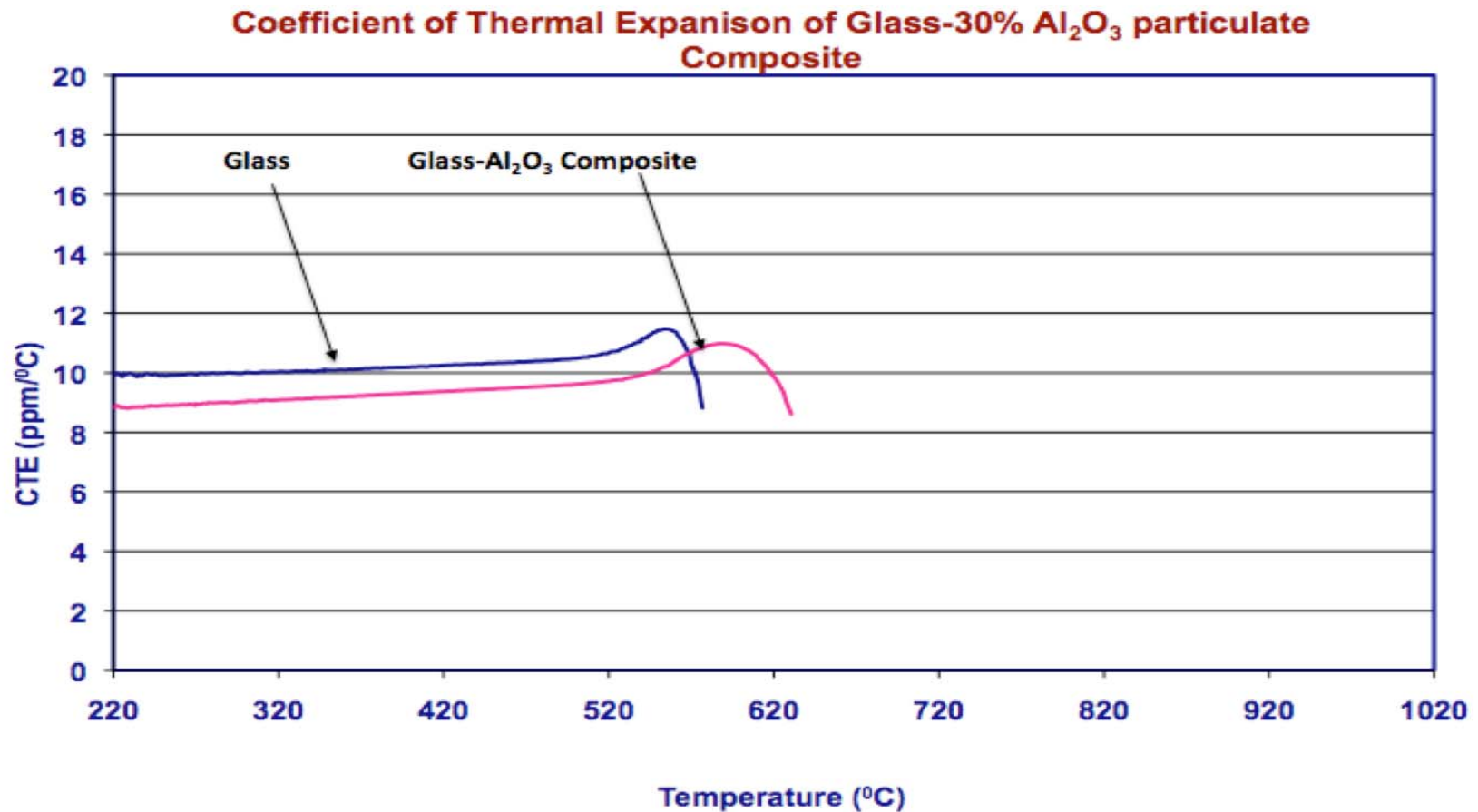
- ◆ YSZ-Electrolyte and Filler-Glass Composites Fabricated by Tape Casting and Sintering

- **Characterize Stability of the Self-Healing Glass-Composites**

- ◆ Thermal Expansion by Dilatometer Between 25-800°C
- ◆ Effect of Annealing in Air and Fuel for 1000h at 800°C
- ◆ X-Ray Diffraction for Stability Against Crystallization Upon Annealing
- ◆ Stability of Glass-Composite in Contact with YSZ
- ◆ Down Select Most Promising Filler for Phase II and Long-Term Stability Studies



CTE OF GLASS-ALUMINA COMPOSITE

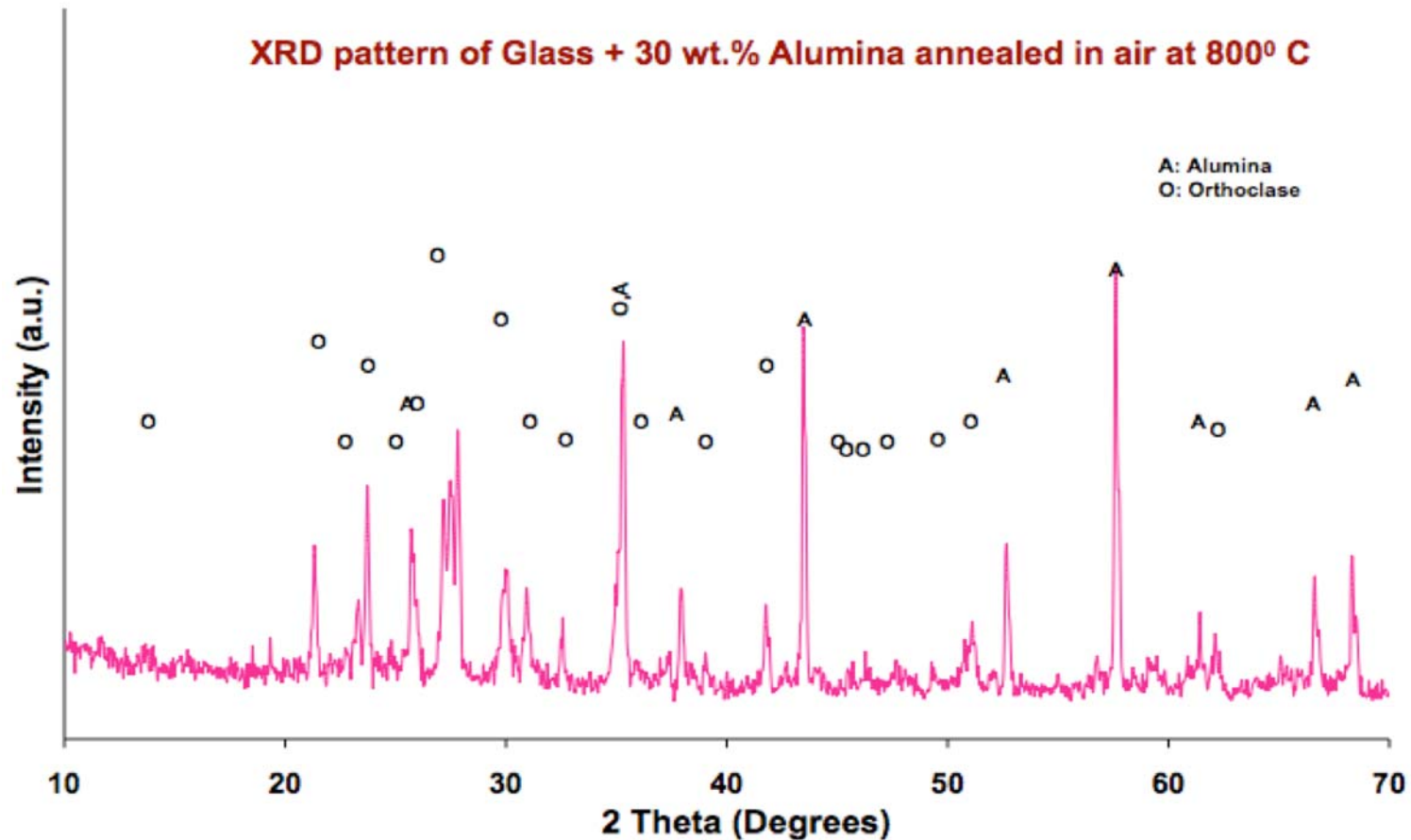


- Lower CTE compared to glass (orthoclase formation)

Raj Singh-2011



STABILITY OF GLASS-ALUMINA COMPOSITE

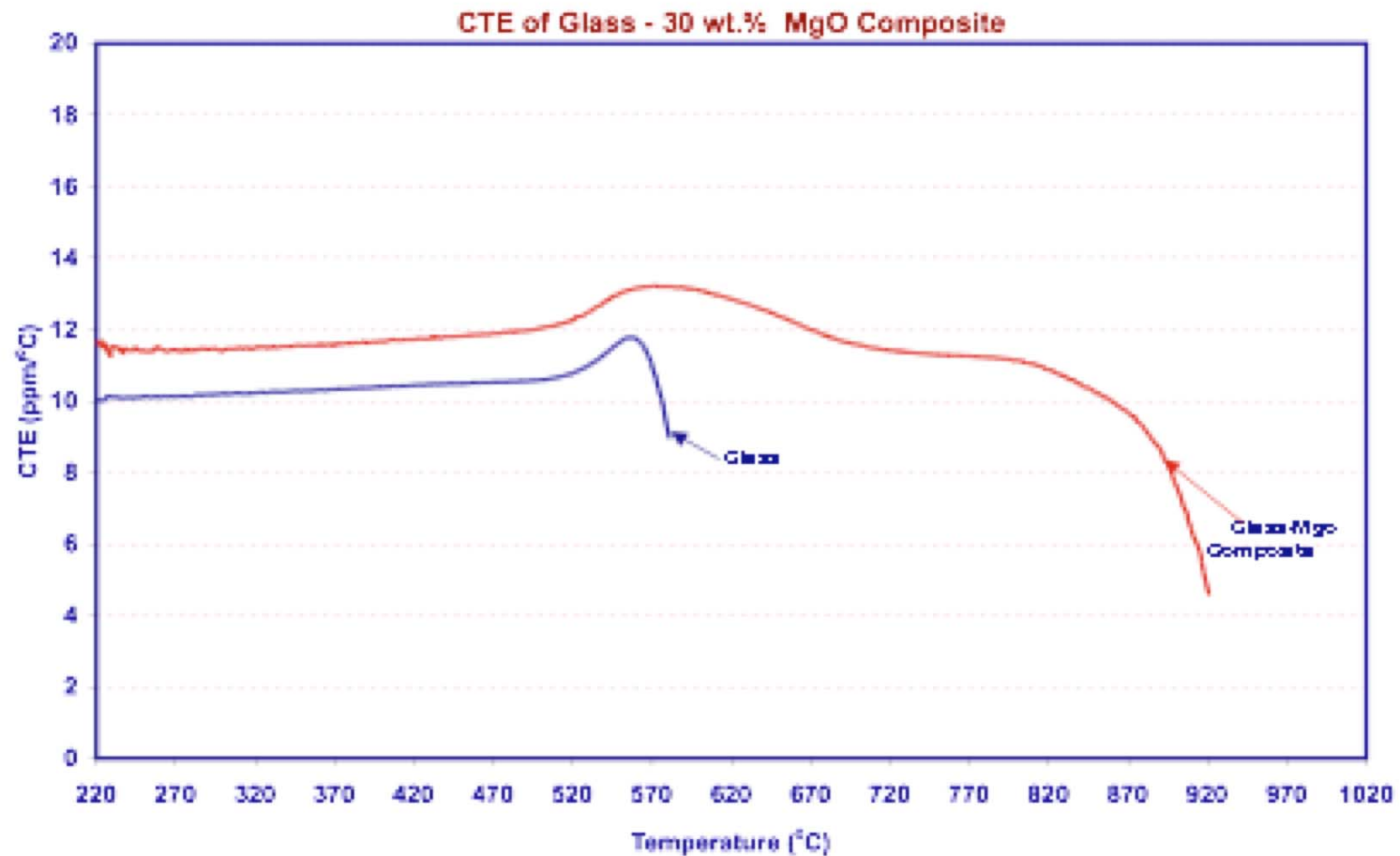


- Reaction of glass with alumina

Raj Singh-2011



CTE OF GLASS-MgO COMPOSITE



- Higher CTE compared to glass but broad behavior [Mg_2SiO_4 (Forsterite)]

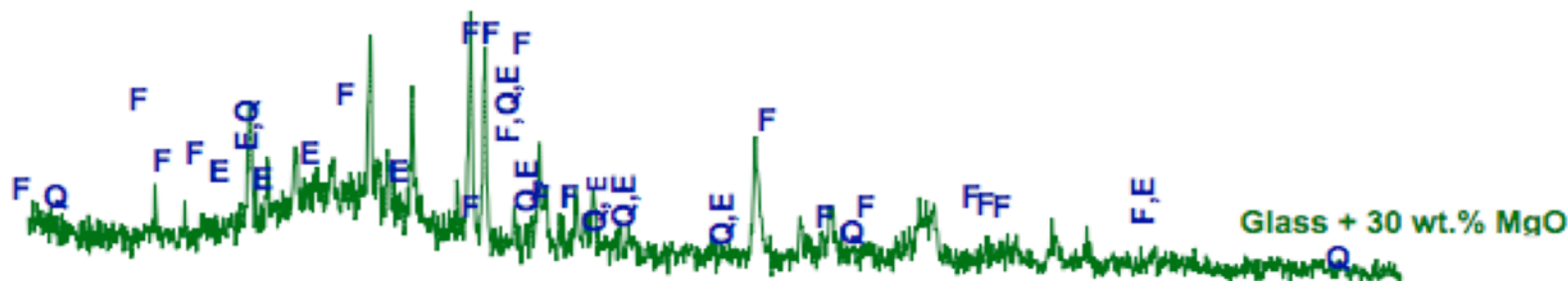
Raj Singh-2011



STABILITY OF GLASS-30%MgO COMPOSITE

XRD Pattern of Glass-30%MgO Composites-As Sintered

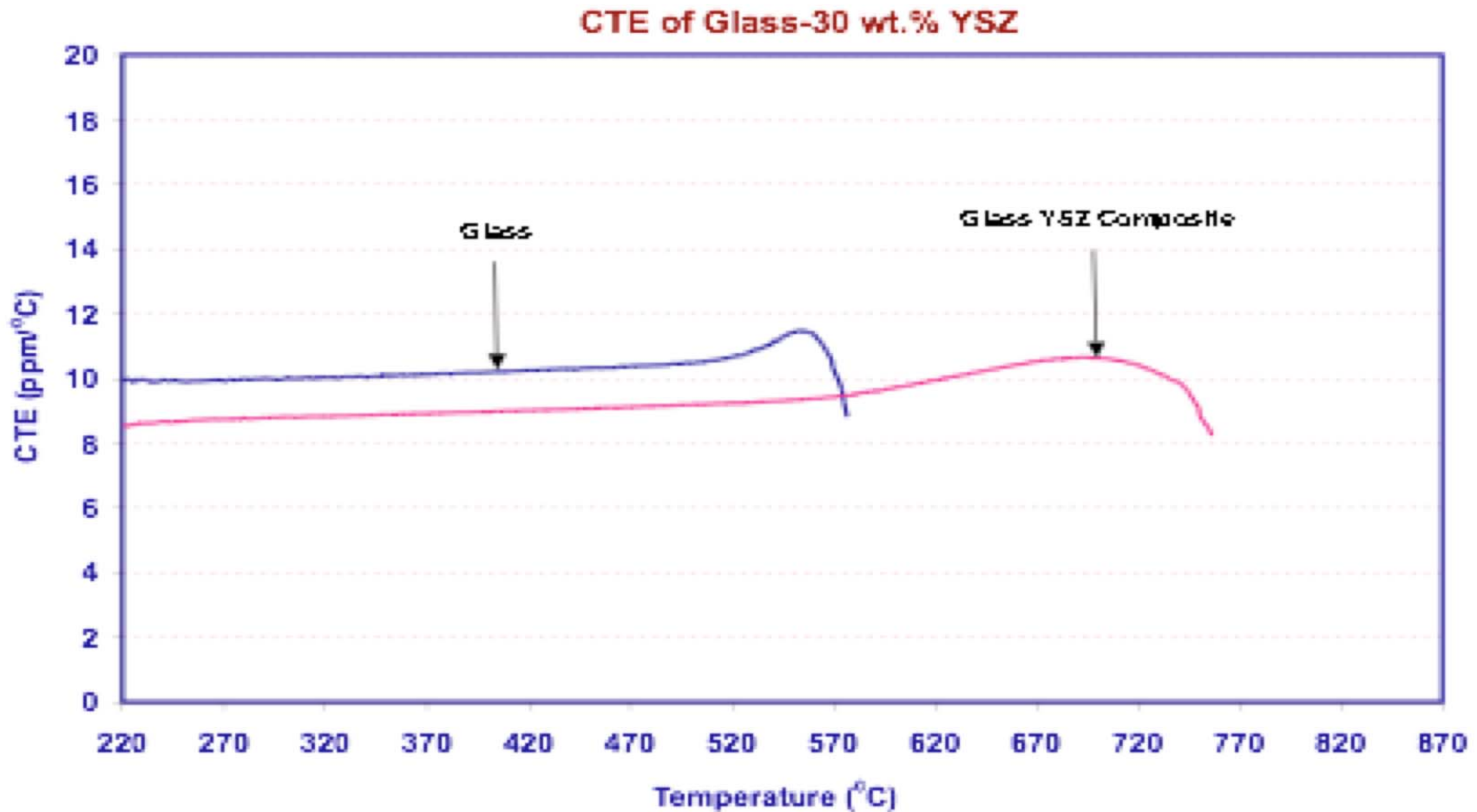
P MgO (Periclase): JCPDS File No. 87-0651
F Mg₂SiO₄ (Forsterite): JCPDS File No. 34-0189
E MgSiO₃ (Enstatite) : JCPDS File No. 85-2494
Q Quartz (high syn) : JCPDS File No. 87-0703



- ## ● Reaction and formation of Magnesium Silicates



CTE OF GLASS-YSZ COMPOSITE

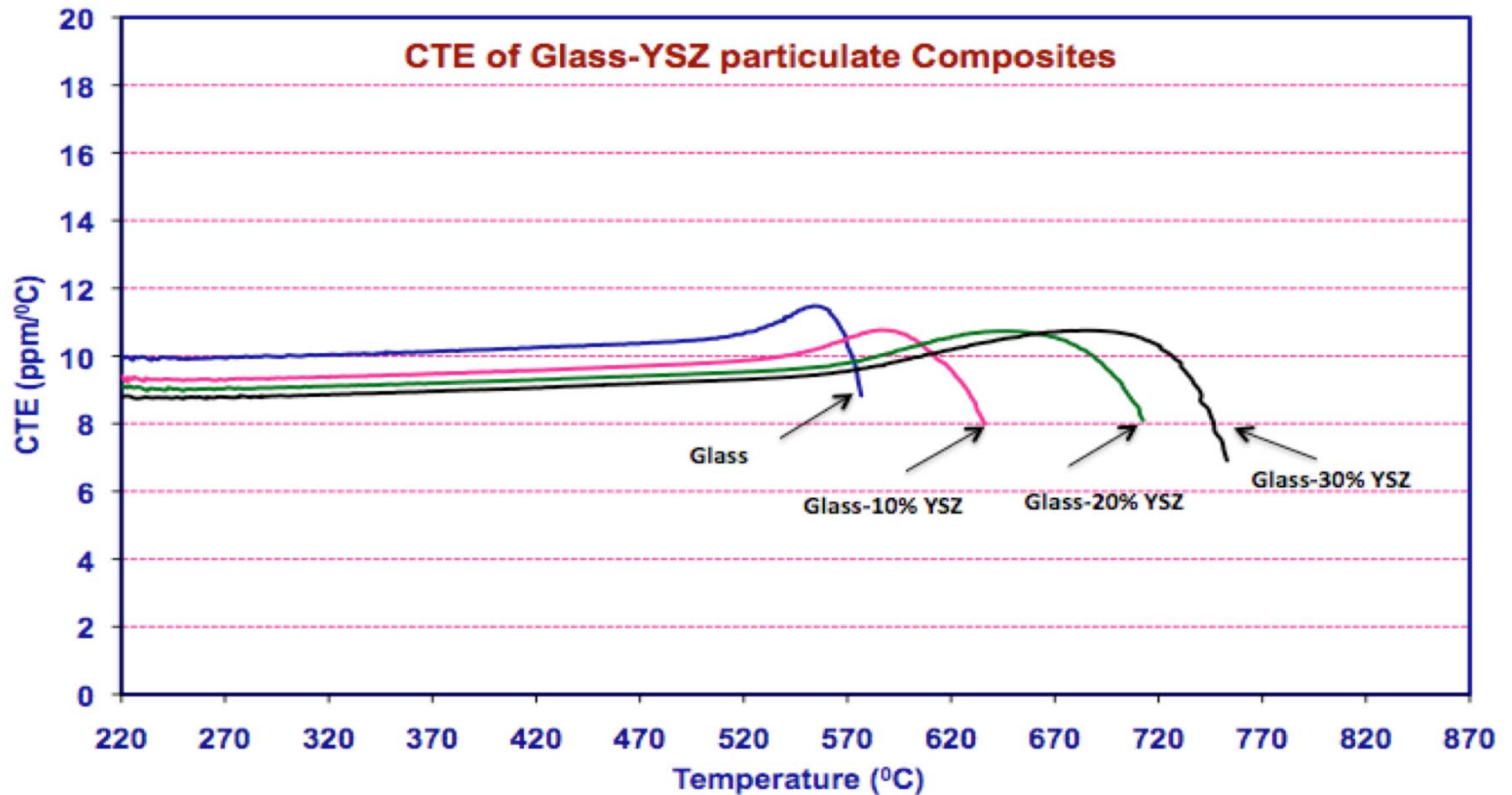


- Lower CTE compared to glass and stable against reaction

Raj Singh-2011



CTE OF GLASS-YSZ COMPOSITE

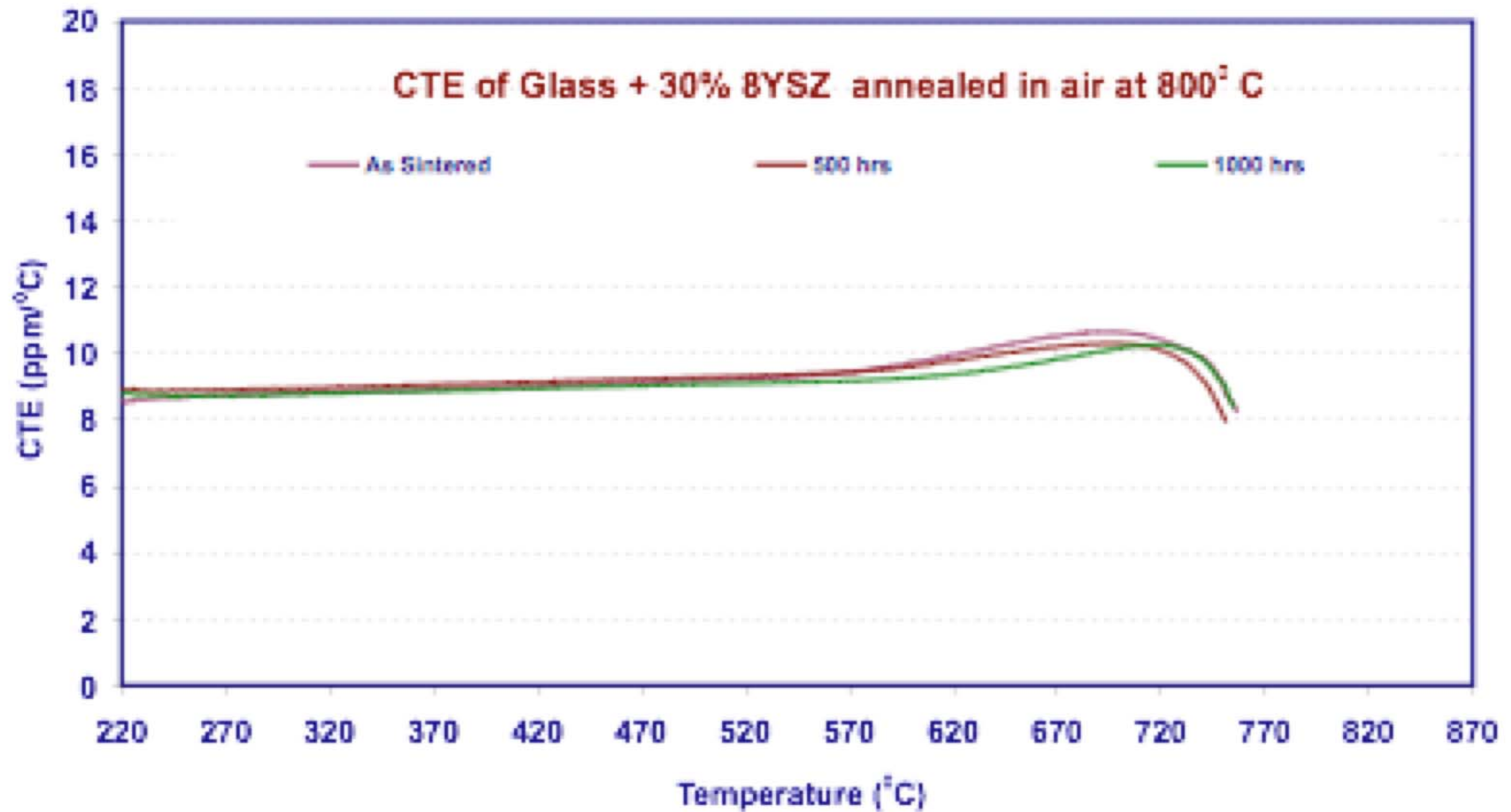


- CTE, glass transition and softening behaviors can be modified

Raj Singh-2011



STABILITY OF GLASS-YSZ COMPOSITE

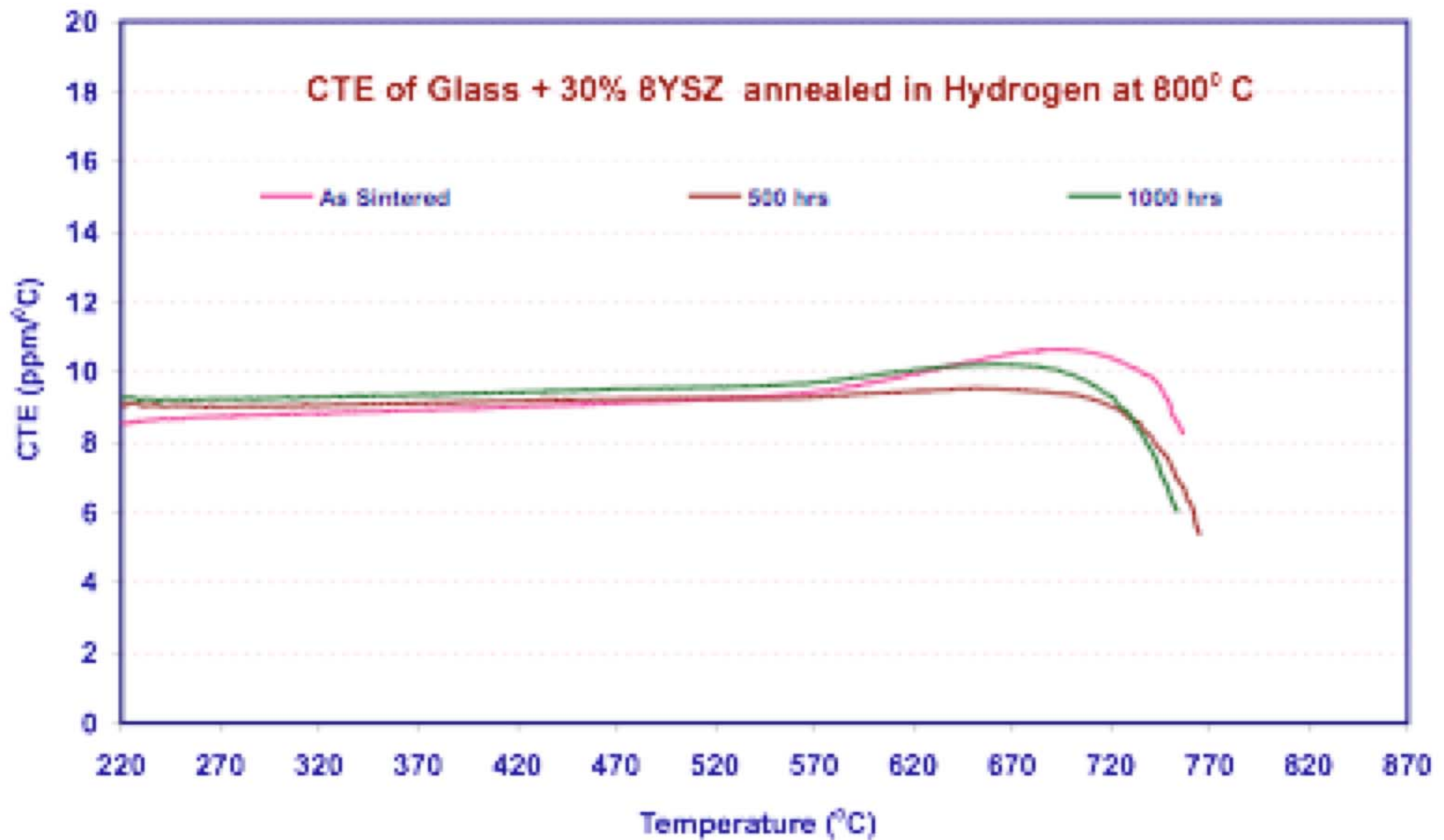


- Insignificant change upon annealing in air for 1000 h

Raj Singh-2011



STABILITY OF GLASS-YSZ COMPOSITE

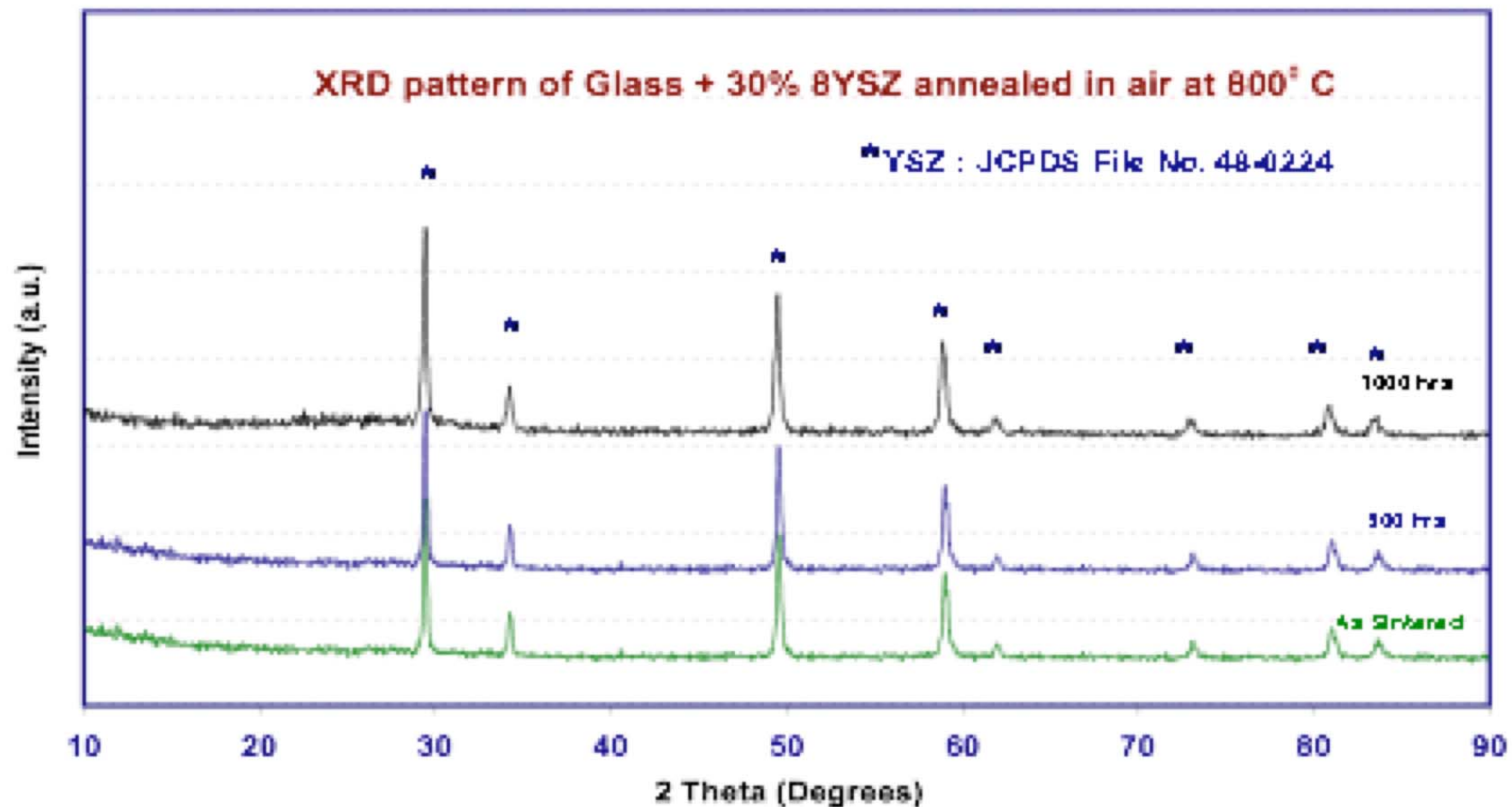


- Insignificant change upon annealing in hydrogen for 1000 h

Raj Singh-2011



STABILITY OF GLASS-YSZ COMPOSITE

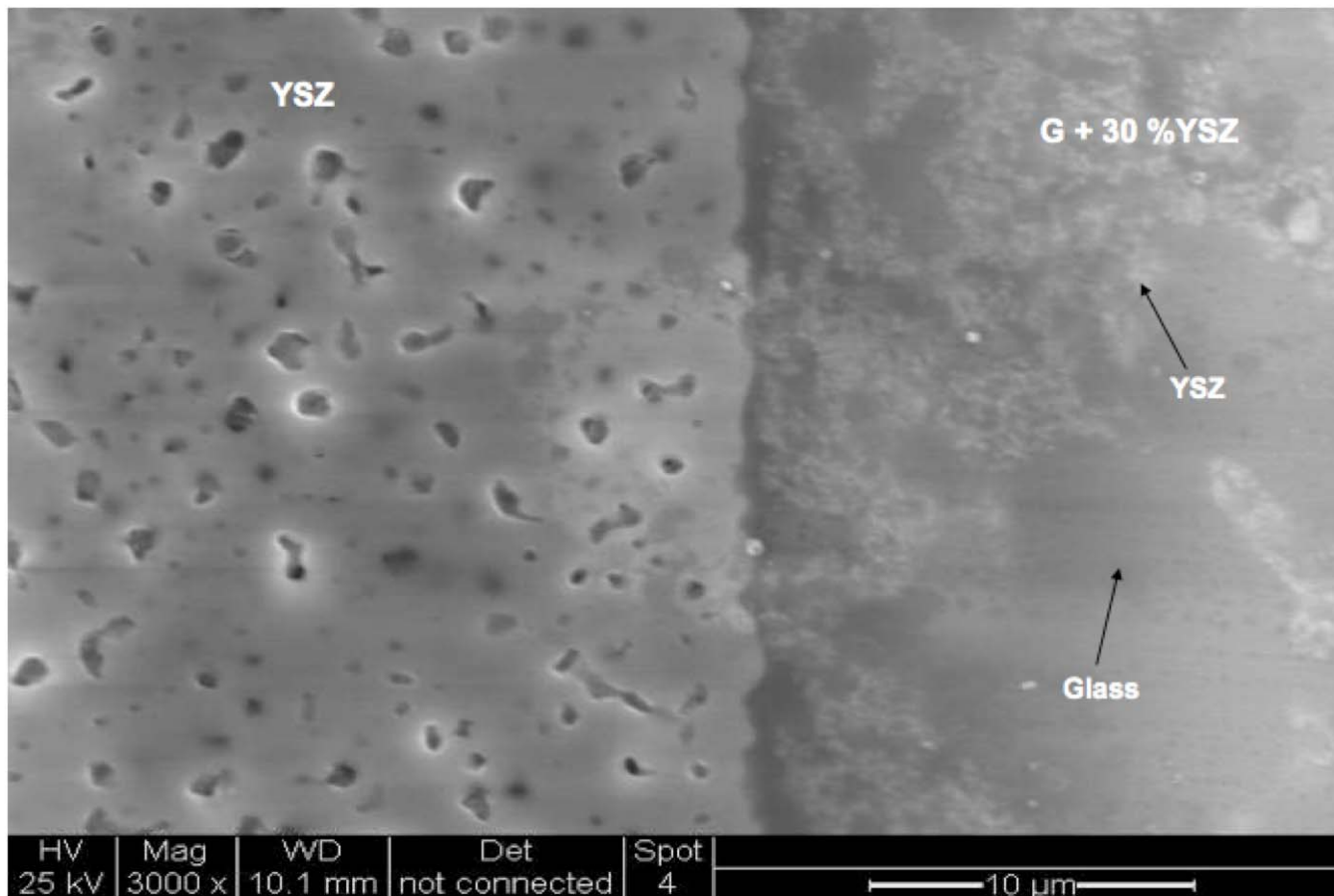


- Insignificant change upon annealing in air for 1000 h

Raj Singh-2011



INTERFACE STABILITY OF GLASS-YSZ COMPOSITE



- No reaction of glass with YSZ upon annealing at 800°C.

Raj Singh-2011



SUMMARY

- A self-healing sealing concept is further advanced for SOFC to satisfy significant thermochemical and thermomechanical incompatibilities among materials requiring hermetic seals. In particular, emphasis of the current program is to find suitable filler materials that can be used to modify glass properties to avoid excessive flow of the sealant.
- Glass-composites with Al_2O_3 , MgO , and YSZ fillers were fabricated to assess their role on thermomechanical behavior. Stability of the reinforced glasses were measured by x-situ experiments at 800°C to demonstrate stability.
- Alumina and MgO fillers reacted with the glass and found to be unsuitable as fillers. YSZ appeared stable and is a more promising filler material. Stability of the glass-YSZ filler composites was determined by annealing samples to 1000 hours in fuel and air environments. Stability is demonstrated for 1000 hours so far.
- Long term stability is expected to demonstrate promise of the self-healing glass-composite seals for potential applications in SOFC.



FUTURE PLANS

- **Phase II: April 2011-September 2012**

- ◆ Down-select self-healing glass-composite from Phase I and determine longer term stability in SOFC environments up to 2000 hours
- ◆ Measure thermomechanical properties of glass-composites after longer term exposure in SOFC environments
- ◆ Characterize glass-composites by expansion, glass-transition, and x-ray diffraction measurements
- ◆ Determine stability of glass-composites in contact with YSZ over extended periods and characterize by SEM
- ◆ These results are expected to provide great promise towards meeting SECA goals of stable seals for SOFC.



Thank You !